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PARAMAGNETIC RESONANCE EFFECT IN VISCOELASTIC MATERIALS

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BACKGROUND

As a result of NASA support during the past two years, particularly in regard to the basic experimental equipment, we have established that Electron Paramagnetic Resonance (EPR) can be used to study several aspects of mechanical failure in polymers. Systematic efforts have been undertaken in a number of these areas and useful quantitative information has been obtained.

Indeed, the initial results have proven so successful that our basic program has been reinforced and expanded into related areas with the assistance of other agencies. For example, the National Science Foundation is supporting an investigation of environmental effects upon polymers, such as stress crazing and cracking, and also an EPR investigation of damage during impact and shock loadings. In addition, the National Institute of Dental Research is sponsoring an EPR investigation of bond rupture in dental materials during decay, grinding, and crushing. These other agencies have expressed appreciation to NASA for the use, on a non-interference basis, of the basic EPR spectrometer purchased under the NASA grant. This combined support has permitted us to structure an integrated program which has generated important synergistic interactions.

OBJECTIVES

The recent interest in the space effort and rocket technology has provided a strong stimulus for research into fracture mechanisms in viscoelastic media. Before this time, the technology was such that the engineer and scientist have not had much to work with in reliably predicting the structural failure of propellant grains and related elements such as fiber reinforced cases etc. Experimental studies of fracture in the past have been involved primarily with macroscopic measurements of crack growth and rupture. Certainly a basic understanding of fracture involves an understanding in terms of physical models of the molecular mechanisms resulting in fracture. Only through such knowledge and insight can the engineer and scientist optimally design. From a very practical standpoint, such information is essential in order to obtain insight into expected behavior, formulate possible simplifying assumptions in design and analysis, make quantitatively meaningful extrapolations, predict behavior under altered service conditions, "design", synthesize and produce better materials, etc. Such knowledge should be an invaluable tool in planning better and more conclusive fracture experiments of all types.

There has been no dearth in theories as to what occurs on an atomic level. Most of these are built upon the various facets of rate processes theory. The largest problem in this area has been in the lack of experimental techniques which can critically test the theories on the atomic level. It is in this area that electron paramagnetic resonance is making a valuable contribution. EPR is a type of absorption spectroscopy capable of detecting unpaired electrons such as result from the scission of covalent bonds. Such bonds are found in polymer chains like those present in all plastics and many propellants.

These unpaired electrons in polymers, often called free radicals, can be generated by chemical attack, irradiation damage or by mechanical degradation, i.e. crushing, grinding, machining or tensile loading. EPR provides a powerful means of investigating these type of degradation processes. Monitoring the signal intensity makes it possible to determing the number of broken bonds and the spectra shape gives valuable clues as to which bonds are being ruptured. In short, out study can be described as: how many, at what rate of which bonds are broken during fracture. Being more specific, the immediate goals we had set for ourselves were:

1. Investigate the spectra and determine which bonds rupture during fracture.
2. Determine the activation energy associated with bond rupture, i.e. the temperature dependence of scission.
3. Determine the effect of stress in lowering the activation energy.
4. Investigate loading or deformation rate and time effects on rate of bond rupture for monotonic loadings in polymers.

5. Investigate the kinetics of bond rupture during cyclic loading or fatigue in polymers. The servo-controlled hydraulic loading system that has been designed and built around the EPR apparatus will allow the application of almost any programmed loading (strain can be similarly controlled if desired), including cyclic up to approximately 1000 cycles per minute. The early work in this area is of particular interest to us because it is in general agreement with a model developed earlier by Williams in the related NASA Grant NGR 45-003-029. These studies should tie in well with macroscopic studies of damage accumulation during fracture and fatigue.
6. Investigate the use of a WLF type temperature shift in broken bond accumulation during fracture. While this type formulation was originally developed to explain viscoelastic stress-strain behavior, it has received quite wide success in fitting such other phenomena as fracture. It is felt the shift factor may also apply for bond rupture and hence for immediate practical data interpretation and use.

RESULTS

Some of our significant findings which relate specifically to the NASA objectives include:

1. Strong EPR signals are obtained during tensile fracture of a number of different highly drawn polymer fibers: Nylon 6, Nylon 6.6, polyethylene, and polyester. Note that this is not the case for cast, extrusion molded materials, etc. This finding indicates that materials engineering may have to include other factors besides chemical similarity when synthesizing the material.

2. Strong EPR signals are obtained during such mechanical degradation as grinding, machining and slicing in every polymer studied. Besides those listed under (1) above, our studies have included PMMA, PVC, polystyrene, Solithane 113, polypropylene, polytetrafluoroethylene, and others.

3. We have found that the Zhurkov and other existing rate process models of bond rupture can not generally be fit to our data. Such models can be made to fit constant stress rate data quite well, but fail very markedly with other loadings such as creep. On a pseudo-empirical basis, however, it was determined that our data was satisfied by a functional relationship of the form

$$C_{ss} = \alpha \exp\{(\beta\sigma-\gamma)/kT\}$$

where C_{ss} is the steady state concentration of ruptured bonds, α is a constant related to the atomic vibrational frequency, γ is the activation energy associated with a c-c bond and β is an activation volume related to the bond elongation. The paper to be presented at the International Fracture Conference gives more details on this aspect of the bond rupture as well as some possible correlations with Zhurkov's results. β was found to be 4.32×10^{19} wich pounds and β 2.28×10^{-24} in.^{3} for Nylon 6.6 fibers.

4. The free radicals produced in Nylon 6 were identified to be at the site

$$- NH - \dot{C}H - (CH_2)_4 - CO -$$

This radical does not represent main chain scission and is likely not formed directly by the internal bond rupture but is thought rather to result from radical suggestion. Careful studies at low temperature resulted in radicals identified as being due to the rupture of the bond.

$$(- NH - CO - CH_2 - \wr - (CH_2)_4 -)$$

5. Dependence of primary bond rupture on strain rate and stress rate have been measured. Preliminary measurements indicate that as these rates increase the number of bonds required to fracture the specimen also increase. At very high rates there is some indication that it may go through a maximum; such results are not conclusive however.
6. EPR has been used to investigate the accumulation of damage during cyclic loading. Attempts to fit a Zhurkov type relation with the constants determined from constant stress rate tests were partially successful in that it did predict the general trends.

OBJECTIVES AND RESULTS IN THE RELATED PROGRAMS

As noted previously, National Science Foundation is supporting work using these techniques to study stress crazing and other surface and environmental effects on fracture. Some of the results of these studies might be relevant to NASA objectives and goals. A few of these results are:

1. Ozone induced cracking in rubber results in strong easily detectable EPR signals. Free radicals formed under the combined influence of uniaxial tensile stress and ozone were found to be quite stable. The initial rate of bond rupture was found to be approximately proportional to ozone concentration at a fixed strain. A threshold strain of approximately 3% was found below which no effect of the ozone environment was detected. EPR is apparently a very sensitive means of studying such degradation. It could quite probably be used to study similar environmental and aging effects in solid propellants and other polymers, as for example smog attack on automobile tires.
2. Studies of new surfaces formed by fracture on a number of semicrystalline polymers indicate that the number of broken bonds is more than an order of

magnitude less than one would expect a plane passing through the cross section of the sample to cut ($\sim 10^{13}$ compared to $\sim 3 \times 10^{14}$). The crack surface apparently selects a path about the michelle that requires roughly 10 times fewer broken bonds than were it to pass through these small crystallites.

3. Above the glass transition temperature the number of broken bonds per unit new surface formed drops off rapidly.
4. Most bonds that are broken in these polymers lie within a couple of microns of the fracture surface.
5. A systematic study of free radical lifetime at various temperatures is well underway. Such information is essential in accurately interpreting all our results, including those of NASA.
6. Work has begun on a model of fracture that relates this phemomena through rate process theory to random lengths of tie chains between crystallites in semi-crystalline polymers.

Research under National Institute of Dental Research sponsorship in investigating the use of EPR for research in teeth and dental materials has been largely involved with the following:

1. An EPR study of dental decay, involved largely with the number of bonds broken as a function of activity, position-relative to decay tooth interface, etc. The effects of various dental medicaments is also being studied.
2. X-ray damage to tooth material.
3. An investigation of grinding mechanisms, bonds broken as function of grinding speed pressure, burr type, etc.

As witnessed by the attached titles of abstracts of papers and reports, EPR has already yielded considerable information and enlightenment in most of these areas. This past success has made these investigators very enthusiastic about the methods potential in our future efforts.

LECTURES AND PAPERS

Our coordinated project and its findings have stimulated considerable interest among fracture investigators. During the year we have received a number of invitations to give lectures on our studies before various research groups. These include an invited lecture at the Interagency Chemical Rocket Propulsion Group, October 1968, an invited lecture at the 1969 Polymer Conference Series in Detroit in May 1969, an invited lecture at the Second International Conference on Fracture in Brighton, England, April 1969, an invited lecture at the Mechanical Properties of Polymers session of the American Chemical Society meeting in October 1969. In addition, during the last year we have been invited to give seminars at Carnegie-Mellon University and the Camille Dreyfus Institute for Polymer Research at the Research Triangle Institute, and at the International Congress of Rheology in Kyoto, Japan, in October 1968. Most of the above lectures will be published.

We have also prepared several other papers for publication. Considerable thought has gone into the preparation of these manuscripts and copies of all of them have been submitted to NASA along with a rather comprehensive review of our efforts up to about four months ago in the form of the doctorate dissertation of David K. Roylance. As it would be redundant to rewrite our results for this report, we have listed above the principal findings that we feel are especially significant, and refer the interested readers to the basic publications on file at NASA. Additional copies can, of course, be obtained from our files.

As a matter of convenience, the Appendix lists all reports, papers, etc. dealing with EPR which were prepared by our group, along with their abstracts.

CONCLUSIONS

We would like to express our sincere thanks to NASA for the support which initiated all these studies. Besides the two professors as principal investigators who have gained much in knowledge and experience from these studies, one other professor, a dentist, a research engineer, and seven students have benefited from the availability of this equipment. Three of the graduate students have also received financial support from the NASA grant.

Appendix

LISTING OF REPORTS AND PUBLICATIONS

1. "Paramagnetic Resonance Effect in Viscoelastic Materials," K. L. DeVries and M. L. Williams, UTEC DO 67-049, Semi-Annual Progress Report, NASA Grant NGR 45-003-037, 1 January 1967 - 30 June 1967, 1 July 1967.

   During the period covered by this grant, the EPR equipment has been purchased, received, and put into operation. A variable temperature accessory has been installed that makes it possible to maintain and control the temperature at any value between -185°C and +300°C. Facilities have also been constructed to control the atmosphere of the sample in the microwave cavity. A hydraulic loading frame, pump, controls, etc. have been designed and constructed for tensile loading the samples in the microwave cavity. Load, strain, and EPR spectra can be simultaneously recorded on a built-in oscillograph system. The experimental set up is illustrated in Figure 1. This report will describe some of the early results obtained in studying fracture mechanisms with this equipment and apparatus.

2. "An EPR Investigation of Newly Formed Fracture Surfaces," K. L. DeVries and M. L. Williams, Presentation to 14th Sagamore Army Materials Research Conference, Raquette Lake, New York, August 22-25, 1967, UTEC DO 67-006, August 1967 (to appear in Proceedings). (NASA/NSF)

   Electron paramagnetic resonance is used to study the free radicals formed during mechanical fracture and γ-irradiation. The experimental results are reported herein. An identification of the free radicals is given and the rate of recombination and the rate of reaction with oxygen discussed. Preliminary tensile fracture data for drawn Nylon 6 fibers is also included.

3. "Some Preliminary Measurements of Free Radical Formation in Polymers Under Stress," K. L. DeVries, D. K. Roylance, and M. L. Williams, Presentation to 6th ICRPG Working Group on Mechanical Behavior, Pasadena, Calif., December 4-6, 1967, UTEC DO 67-026, December 1967. (NASA)

   It is proposed to present some initial observations on the use of electron paramagnetic resonance to detect the number of free radicals formed in polymeric materials due to the application of tensile stress. A summary of pertinent theoretical background, including the pioneer work of Zhurkov will be followed by our initial results showing the signatures and decay rates obtained in two materials, drawn Nylon and Solithane 113 for three types of damage to the specimens -- crushing, radiation, and stretching.

4. "Stress Crazing in Plastics," K. L. DeVries and M. L. Williams, UTEC DO 67-086, Annual Progress Report, NSF Grant GK-1376, 1 December 1967.

EPR techniques are being used to investigate fracture mechanisms in polymeric materials with particular attention to environmental and surface effects. Through this detection of free radicals, it should be possible to determine not only the number, but which bonds are broken during various mechanical type failures in covalently bonded materials. An EPR Spectrometer has been received (purchased by funds from other sources), set up, and put into operation. Accessory equipment has been designed, and partially constructed and assembled. This equipment includes from -190°C to +300°C. A loading system has been constructed (a servo control system is presently being added to this system) that when completed will be capable of constant load or strain, constant load or displacement rate, as well as various programmed loadings. A systematic study of fracture is under way using this equipment. Some interesting and significant findings have already been made, as are outlined later in this report and in our paper at the Sagamore Materials Conference.

5. "Fracture in Dental Materials Using EPR," M. L. Williams and K. L. DeVries, UTEC DO 67-085, Annual Report, NIDR Grant DE 02615, 5 December 1967.

EPR studies have been conducted on dental enamel, dentin, collagen, gelatin, artificial tooth (PMMA), PMMA tooth filling material (Severitron), PMMA base material (Lucitone), PMMA base repair material (Long's Repair Acrylics), and epoxy resin Araldite 502 to shed light on the fracture mechanisms in these polymers. The mechanical degradation has been correlated with that of γ-irradiation using EPR technique. The mechanical degradation has been investigated by grinding these polymers, when applicable, in liquid nitrogen and recording their EPR spectra at -160°C. Mechanical degradation results in the breaking of polymeric bonds, giving rise to free radicals which are recorded spectrometrically. Different spectra are obtained for dental enamel, dentin and collagen. Spectra of gelatin is similar to collagen with some deviation. Spectra of dental polymeric materials are more or less the same with the exception of PMMA tooth filling material in which case two new peaks appear. The formation of different EPR spectra has been discussed and where possible the free radical responsible for this spectra has been detected.

6. "Paramagnetic Resonance Effect in Viscoelastic Materials," K. L. DeVries and M. L. Williams, UTEC DO 68-008, Semi-Annual Progress Report, NASA Grant NGR 45-003-037, 1 July 1967 - 31 December 1967, 1 January 1968.

7. "An Investigation of Basic Fracture Mechanisms Using EPR," K. L. DeVries, D. K. Roylance, and M. L. Williams, UTEC DO 68-056, 15 July 1968.

   Using EPR, it has been possible to determine how many of which bonds are broken during fracture and to monitor the bond breakage as a function of time. Such studies provide important new insights into the mechanisms and kinetics of the fracture process. From an analysis of the EPR spectra and correlation with other results in the literature, it was deduced that the primary fracture points in Nylon 6 are the c-c bonds occupying β-positions with respect to the amide groups.

8. "An EPR Investigation of Polymer Fracture," D. K. Roylance, UTEC ME 68-059, Ph.D. Dissertation, Mechanical Engineering Department, University of Utah, August 1968.

   Electron paramagnetic resonance (EPR) spectroscopy is a form of microwave absorption spectroscopy in which transitions are induced between the Zeeman energy levels or unpaired electrons. Since bond breakage in polymers results in the production of unpaired electrons, or free radicals, EPR spectroscopy can be used to study the submicroscopic mechanisms of fracture in these materials. Using EPR techniques, bond breakage induced by γ-irradiation and grinding as well as uniaxial tension has been studied for a number of polymers. It has been possible to determine how many of which bonds are broken during fracture and to monitor the bond breakage as a function of time so as to provide important new insights into the mechanism and kinetics of the fracture process. Highly crystalline, oriented fibers have proven most amenable to EPR analysis during tensile fracture and this paper presents tensile data taken on drawn polycaprolactam (Nylon 6) and polyethylene fibers.

   From an analysis of the EPR spectra and correlation with other results in the literature, it was deduced that the primary fracture points in Nylon 6 are the c-c bonds occupying β-positions with respect to the amide groups. Free radical concentrations in this material reach approximately 10^{17} spins per gram at fracture and follow kinetics which seem to imply that presently existing theories of bond rupture are oversimplified. Although the kinetics of free radical formation are complex, a correlation between stress and the steady-state free radical concentration was found which took the form of a thermally-activated stress-aided process.

9. "Fracture Detection in Polymers by Electron Paramagnetic Resonance," D. K. Roylance, K. L. DeVries, and M. L. Williams, For presentation at 2nd International Conference on Fracture, Brighton, England, April 13-18, 1969, UTEC DO 68-069, 31 August 1968. (NASA/NSF)

Electron paramagnetic resonance (EPR) spectroscopy is a form of microwave absorption spectroscopy in which transitions are induced between the Zeeman energy levels of unpaired electrons. Since bond breakage in polymers results in the production of unpaired electrons, or free radicals, EPR spectroscopy can be used to study the submicroscopic mechanisms of fracture in these materials. Using EPR techniques, bond breakage induced by uniaxial tension has been studied for a number of polymers. It has been possible to determine how many of which bonds are broken during fracture, and to monitor the bond breakage as a function of time so as to provide important new insights into the mechanism and kinetics of the fracture process. Highly crystalline, oriented fibers have proven most amenable to EPR analysis during tensile fracture, and this paper presents tensile data taken on drawn polycaprolactam (Nylon 6) fibers. Free radical concentrations in this material reach approximately 10^{17} spins per gram at fracture (in this case number of free radicals present). The kinetic behavior seems to imply that presently existing theories of bond rupture are oversimplified. Although the kinetics of free radical formation are complex, a correlation between stress and the steady-state free radical concentration was found, however, which took the form of a thermally-activated stress-aided process.

10. "Fracture in Dental Materials Using EPR," K. L. DeVries and M. L. Williams, UTEC DO 68-078, Annual Report, NIDR Grant DE 02615, 31 August 1968.

Since October 1, 1967, the University of Utah has been conducting a study of microscopic mechanisms relating to failure of dental materials using an electron paramagnetic resonance (EPR) spectrometer. Our preliminary results indicate that the use of EPR methods will materially help in understanding the microscopic fracture mechanisms in dental materials which occur during grinding, mechanical loading, x-ray penetration, and biological decay.

11\. "Electron Paramagnetic Resonance Measurement of Strain Rate and Cyclic Effects on Bond Rupture," M. L. Williams and K. L. DeVries, Presentation to 5th International Congress of the Society of Rheology, Kyoto, Japan, October 5-19, 1968, UTEC DO 68-083, September 1968. (NASA/NSF)

Electron paramagnetic resonance (EPR) techniques to study free radical generation in solids has been used to examine the applicability of the original Zhurkov formula for bond breakage, $dN_b/dt \doteq B \exp(\alpha\sigma)$, during constant stress, constant stress rate, and low cycle fatigue loading. Correlation was found for constant stress rate and qualitative agreement for the other loadings. A careful study of the history of the radical concentration, rather than solely the fracture lifetime, is recommended as a key to guide further theoretical developments.

12\. "An Atomic Approach to Fracture of Polymers," K. L. DeVries and M. L. Williams, Presentation to 7th ICRPG Working Group on Mechanical Behavior, Orlando, Florida, November 13-15, 1968, UTEC DO 68-073, 15 September 1968. (NASA/NSF/NIDR)

The field of rocket tecnology has stimulated research into the mechanisms of fracture in viscoelastic media. This is particularly true for fracture in polymers, where the engineer and scientist is faced not only with the problem of structural failure of the propellant grain itself, but also related structural elements such as the fibers of reinforced plastic shells. One can approach the fracture phenomenon from two distinctly different points of view, either the submicroscopic (atomic) approach, or the macroscopic standpoint. In the atomic approach one attempts to relate external loadings to molecular forces which in turn result in chemical bond rupture. The accumulation of these broken bonds then leads to the final gross fracture of the specimen or engineering element. In the macroscopic approach the material is normally treated as a continuum or at least a quasi-continuum with mathematically introduced flows or holes, and the emphasis is placed on devising some functional relationship such as an energy balance or statistical analysis of crack nucleation or growth dealing with the local stress and/or strain in the material. Certainly this latter approach has received the most attention in engineering analysis. It allows the prediction of failure for specific loadings and provides the engineer with a generally satisfactory design tool. However, a basic understanding of fracture involves an understanding, usually in terms of a physical model, of the molecular mechanisms. Such an understanding is important to the engineer and materials scientist from a very practical standpoint. Only through such an understanding is it possible to: obtain insights into expected behavior, possibly simplifying assumptions in design and analysis, make quantitatively meaningful extrapolations, predict behavior under altered service conditions, etc. as well as better planned experiments.

12. (contd.)

Until very recently most investigations of polymer strength at the microscopic level have been wholly theoretical in nature. The bulk of these approaches has been based largely on Rate Process Theory, and specialized to the case of uniaxial tension. In this latter case, bond breakage is treated as a statistical phenomenon in which the applied stress lowers the activation energy of the bond. The authors of such theories have been able to claim a certain amount of agreement with macroscopic experimental observations. It might be argued, however, that when two, three, or more adjustable parameters are available, many alternate reasonable models might accommodate a given set of experimental data.

It would therefore appear that improved experimental techniques would be helpful, particularly if these could be related to atomic occurrences. A few such methods are being developed. Knauss is developing an acoustic noise technique which will allow the observation of the rate of rupture of "ligaments" in elastomer foams. Another approach used by Regel, Muinov, and Pozdnyakov and by Andrews and Reed involves the analysis of gases evolved from a polymer during fracture. These gases reportedly originate at the broken ends of polymer chains and are developed as a result of the unpaired electrons at these sites. The method used by the authors permits a direct measurement of atomic bond rupture by measuring free radical concentration using electron paramagnetic resonance (EPR) techniques. It is a direct outgrowth of the original investigations conducted by Zhurkov and his co-workers at Leningrad. This paper will present a brief synopsis of some of the results involving these techniques which have been obtained since the middle of 1967 at the Institute for Materials Research at the University of Utah.

13. "Free Radical Formation During Machining and Fracture of Polymers," D. K. Backman and K. L. DeVries, UTEC ME 68-099, December 1968, submitted for publication. (NASA/NSF)

Electron paramagnetic resonance measurements of the number of free radicals formed during cutting and grinding of polymers are described. It was found in the semicrystalline polymers studied that below the glassy transition temperature about 2 x 10^{13} free radicals are formed per sq cm of surface formed. It is proposed that this number results from the crack progressing selectively through the glassy regions about more ordered regions in the polymers.

14. "The Uses of Electron Paramagnetic Resonance in Studying Fracture," K. L. DeVries, D. K. Roylance, and M. L. Williams, UTEC DO 68-100, December 1968, submitted for publication. (NASA/NSF)

The uses of electron paramagnetic resonance (EPR) in studying aspects of polymer fracture are discussed. The sensitivity of EPR is such that all phases of fracture are not amenable to investigation by these means. This paper attempts to define those areas where the authors' experience would indicate that success might or might not be expected. A discussion of the difference between the tensile fracture of drawn polymer fibers, in which strong signals are obtained, and cast and molded materials is given.

15. "Electron Paramagnetic Resonance Measurements of Strain Induced Ozone Cracking in Rubber," K. L. DeVries, E. R. Simonson, and M. L. Williams, For presentation at the ASME Conference "Environmental Effects in Fatigue of Engineering Materials," Washington, D. C., March 31 - April 2, 1969, UTEC DO 68-103, 5 December 1968.

An electron paramagnetic resonance (EPR) method for monitoring the rate of atomic bond rupture in rubber subjected to uniaxial tensile strain in an ozone environment is described. The free radicals so formed are found to be quite stable and present in large, easily detectable concentrations. The initial rate of bond rupture was found to be approximately proportional to ozone concentration at a fixed strain. Below a prestrain of three per cent, no effect of the ozone environment was detected; above this threshold, the rate of rupture increases with strain up to strains of approximately twenty per cent. It appears that this EPR technique is very sensitive and can yield information not readily obtainable by more conventional techniques.

16. "Paramagnetic Resonance Effect in Viscoelastic Materials," K. L. DeVries and M. L. Williams, UTEC DO 68-109, Annual Progress Report, NASA Grant NGR 45-003-037, 1 January 1968 - 31 December 1968, 1 January 1969.

17. "EPR Investigation of Bond Rupture in Teeth and Dental Materials due to X-Ray Irradiation and Grinding," R. R. Despain, K. L. DeVries, and M. L. Williams, For presentation at 47th Annual Meeting of The International Association for Dental Research and the North American Division of IADR, Houston, Texas, March 20-23, 1969.

Electron paramagnetic resonance (EPR) technique allows the measurement of molecular bond fracture. This paper reports the accumulation of broken polymeric bonds during various types of degradation in dental materials and teeth, including damage resulting from x-rays and grinding.

17. (contd.)

Whole and sectioned teeth were subjected to x-rays of various intensity between 60 and 90 kv and current links between 10 and 15 ma for total dosages up to 100 seconds. For the grinding studies, the effect of burr speed, pressure, cooling, and other factors on number of broken ruptures is discussed.

It appears that in certain cases, EPR can give an important insight into microscopic fracture mechanisms in dental research.

18. "Investigation of Decay with EPR," R. R. Despain, K. L. DeVries, and M. L. Williams, For presentation at 47th Annual Meeting of The International Association for Dental Research and the North American Division of IADR, Houston, Texas, March 20-23, 1969.

Electron paramagnetic resonance (EPR) is an experimental means of measuring microscopic fracture by detecting the concentration of free-radicals in living and inert polymeric materials. In principle, the type of broken chemical bond can also be measured. Carious material was removed from a number of human teeth and subjected to analysis by EPR. Signals, indicative of bond destruction, were detected. The signal intensity was found to be proportional to the activity and extent of decay. Test results showing the effects of certain cavity medicaments on decay activity are also presented.